Relaxation mechanism of ferroelectric switching in $Pb(Zr,Ti)O_3$ thin films

O. Lohse,[a] M. Grossmann, U. Boettger, and D. Bolten
Institut für Werkstoffe der Elektrotechnik, RWTH Aachen, D-52056 Aachen, Germany

R. Waser
Institut für Festkörperforschung, Research Center Jülich, D-52425 Jülich, Germany

(Received 9 May 2000; accepted for publication 16 October 2000)

The polarization reversal process of tetragonal $Pb(Zr,Ti)O_3$ thin films has been intensively studied using conventional hysteresis and rectangle pulse measurements. Decreasing the voltage level of the pulses significantly slows down the polarization switching to the range of milliseconds. The switching current response shows a Curie–von Schweidler behavior over a broad time range. The transient current and the frequency dependence of the $P-V$ loops of these films compared to the properties of ferroelectric single crystals show some similarities but also significant differences. The theoretical models of the classical ferroelectric phase transition and especially the conditions of the pulse measurements in single crystals and thin films are discussed. It leads to the conclusion that it is not the domain wall structure and domain wall motion that determine the polarization reversal but dissipative polarization processes which can take place in both ferroelectric and nonferroelectric high-k dielectric thin films. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1331341]

I. INTRODUCTION

Thin films of perovskite materials such as lead zirconate titanate (PZT)[1] and layered perovskites such as strontium bismuth tantalate[2] are being intensively studied for their application in high density ferroelectric random access memories integrated circuits.[3] In addition to processing issues of integrating these materials in semiconductor technology, the ferroelectric properties and their reliability are still of major interest. Imprint, fatigue, and retention are the most investigated subjects. But in comparison to nonferroelectric barium strontium titanate (BST), where the dielectric relaxation has been extensively explored,[4] relaxation in ferroelectric materials has not yet received the attention it deserves. In this work, well developed measuring techniques based on conventional hysteresis measurements and voltage step characterization are exploited to elucidate the origin of relaxation in ferroelectric materials for the fast read and write access of the memory cell.

The switching time of the reversal in ferroelectric thin films is assumed to be below nanoseconds,[5,6] but only when high voltage levels are applied, e.g., 5 V for PZT thin films of 200 nm thickness. For low voltage levels, the switching process can be very slow and this is of great interest for the application in fast access memories, since it can, in principle, limit the access time of the memory cell, especially in the desired low voltage operation range.

II. POLARIZATION REVERSAL IN SINGLE CRYSTALS

The inversion process in single crystals has already been intensively investigated by direct observation of domain wall formation and movement. In $BaTiO_3$ single crystals, e.g., Merz,[7,8] Fatuzzo,[8] and Fousek *et al.*[9] have found that the polarization reversal happens by forming of opposing 180° or orthogonal 90° domains in the shape of needles and wedges. The resulting maximum displacement current i_{max} was measured as a function of the applied field and can be fitted by the empirical law

$$i_{max} = i_0[\exp(-\alpha/E)], \tag{1}$$

where i_0 and α (called the ''activation field'') are constants and E is the applied electrical field. A similar empirical law can be found for the switching time t_s, which is the most significant quantity and describes the duration of the polarization reversal

$$t_s = t_0[\exp(\alpha/E)], \tag{2}$$

where t_0 is a constant. The value of α is the same in both Eqs. (1) and (2). More often, it can be found that the switching time is defined as the instant at which the displacement current is at its maximum, e.g., in the work of Pulvari *et al.*,[10] but this merely affects the value of t_0. For an illustration of the definition of i_{max} and t_s, see Fig. 1, which shows the dependence of the switching current on electric field from the paper of Pulvari of single crystal triglycine fluoberyllate (TGFB) and triglycine sulfate (TGS).

Equations (1) and (2) are only applicable when the applied field E is constant during the polarization reversal. In the paper of Merz[7] the evolution of the electrical field is shown during switching and it is clearly visible that the field is, indeed, constant. To achieve this, the time constant of the dielectric charging $\tau_{RC_{diel}}$ must be much smaller than the switching time t_s. In the work of Pulvari,[10] this is also accomplished. The switching current data shown in the paper of Pulvari are very similar to those of the work of Merz, although the domain structure of these materials is different from that of $BaTiO_3$ single crystals. As shown in Fig. 1, the dielectric charging is clearly separated from the polarization switching hump. The time constant of the dielectric charging

[a]Electronic mail: lohse@iwe.rwth-aachen.de

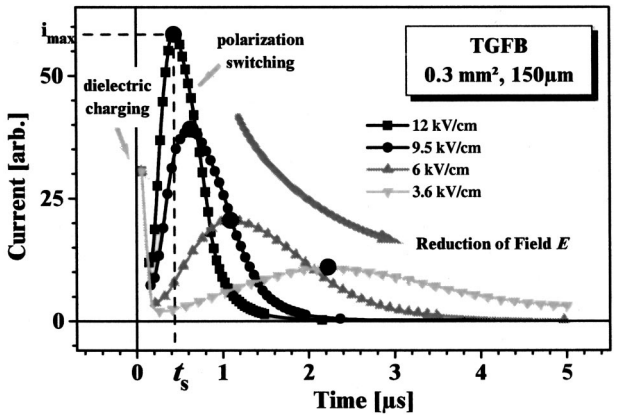

FIG. 1. Polarization switching current of TGFB single crystal with decreasing electrical field (data reproduced after Ref. 10).

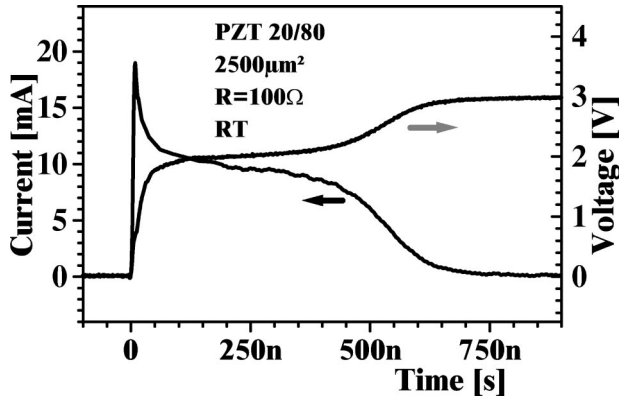

FIG. 2. Switching current and voltage evolution of a pulse measurement with 1 μs width and 3 V level of PZT. The voltage drop across the capacitor is not constant during switching.

is determined by the dielectric capacitance of the sample and the inevitable series resistors due to the internal resistance of the voltage generator, the shunt, and line resistance. By contrast, the switching time is determined by many factors, including the domain structure, the nucleation rate of opposite domains, and the mobility of the domain walls.[11] In polycrystalline materials, the issue becomes yet further complicated due to the microstructure. The requirement that the time constant of dielectric charging be different from the polarization switching time is fundamental since, otherwise, no direct interpretation of the switching behavior is possible. If this condition is not fulfilled, the electrical field is not constant but depends on the experimental configuration, especially the circuit resistance and the dimensions, i.e., the dielectric capacitance, of the sample.

Another way to avoid the problem of an undetermined excitation signal is to apply an alternately increasing and decreasing electrical field, which can be electrically controlled and is independent of the sample and the resistance. This is, in principle, the way $P-V$ are recorded. The hysteresis loop of a ferroelectric capacitor is determined by the polarization reversal process, also. The interpretation of the loop, however, is much more difficult and needs integral calculation methods. Such methods have been successfully developed by the group of Ishibashi.[12–14] They have included the field dependence of the polarization switching and modeled the $D-E$ hysteresis loops depending on the excitation frequency of the triangle as well of the sinusoidal signals and found good agreement to experimental data of TGS single crystals. The loops have been theoretically studied on the basis of the Kolmogorov–Avrami (K–A) model[15–18] extended for the case of applied field dependent sidewise velocity of the domain walls. The K–A is a statistical model which describes the phase transition kinetic in infinite media and was originally developed to model the crystallization process of metals. In ferroelectrics, it can describe the time dependent fractional area $c(t)$ of the switched polarization and reads in a simple form as

$$c(t)=1-\exp[-(t/t_0)^n], \tag{3}$$

with t_0 being mainly determined by the nucleation rate, the wall mobility, and the applied field, and n mainly by the dimensionality of the domains. That this model can be applied for ferroelectric materials has also been supported by the investigations and calculations of Shur,[19] who analyzed the current response of thin plates of single crystal lead germanate $Pb_5Ge_3O_{11}$ and measured the change of the shape of the domains by optical inspection, and the change in the exponent n.

The ferroelectric polarization reversal process and the theory that it is ascribed to the transition of opposite domains seems to be self-consistent for many single crystal materials. It describes the switching data as well as the hysteresis loops very well. But, can it also describe the polarization reversal in ferroelectric thin films?

III. POLARIZATION REVERSAL IN THIN FILMS

As mentioned earlier, the interpretation of the switching current of a ferroelectric capacitor is difficult when it depends on the external circuit and the sample dimensions. For thin films, this is particularly the case since the dielectric charging in a voltage step experiment can not be separated from the polarization switching when the voltage levels applied are significantly higher than the coercive voltage. For example, the pulse measurements performed by Larsen *et al.*[20] showed that the switching time is always of the same order of magnitude as the time constant of the dielectric charging and that the time resolution of the measurement system indicating an inherent switching time of less than 1.8 ns. Typical switching data of a PZT thin film are given in Fig. 2. It shows the current response and the evolution of the voltage across the sample capacitor. It can be clearly seen that the voltage is not constant. The often used approach of subtracting the nonswitching from the switching current response and interpreting it by applying the Merz equations is not possible since the voltage drop across the sample is not constant, in contrast to the precondition for applying the Merz analysis. It has been shown that by using this approach the extracted activation field is not an intrinsic property of the material but is mainly determined by the shape of the hysteresis curve and not by the domain wall kinetics.[21] There are three possible approaches to separating the dielectric charging from the polarization switching. The first is to re-

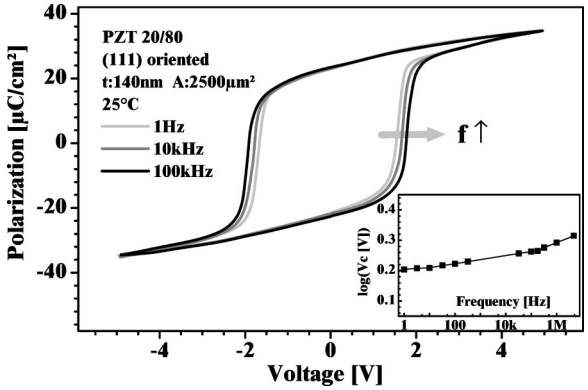

FIG. 3. Hysteresis curves of PZT thin film with different excitation signal frequencies. Inset: log–log plot of coercive voltage V_c vs frequency f.

duce the circuit resistance; but this is limited by the internal resistance of the voltage generator, usually 50 Ω. The second is to decrease the capacitor size, i.e., decreasing the dielectric capacitance; but in addition to damaging the ferroelectric properties due to the integration process, especially etching, the signal to noise ratio of the current response gets worse. And, the third approach is to decrease the applied voltage since, after Merz, a reduction would lead to an increase of the switching time; this has been utilized in this work for PZT thin films.

It is known from many works on ferroelectric thin films that the coercive voltage depends on the excitation signal frequency.[22–24] So additionally in this work, the frequency dependence of the $P-V$ loops of PZT thin films is investigated. As mentioned in Sec. II, the evaluation of the frequency dependent $P-V$ loops is an alternative method to extract information about the polarization switching since in the same way as in single crystals the polarization reversal process in thin films is supposed to affect the coercive voltage and the $P-V$ loops with varying excitation frequency.

IV. EXPERIMENT

The tetragonal PZT thin films were fabricated by a chemical solution deposition on a platinized Si/SiO_2 wafer with a titanium adhesion layer. The precursors, consisting of lead–acetate, titanium–isopropoxide, and zirconium–isopropoxide dissolved in 2-butoxythanol, were deposited by repeating spin on and pyrolysis processes and then the films were crystallized in oxygen at 700 °C. After platinum sputtering, the top electrodes were structured by lift off, and afterwards finally annealed by a rapid thermal annealing process. The thickness is approximately 140 nm, capacitor sizes are 50 μm by 50 μm.

In Fig. 3, the hysteresis loops of the sample are shown at different excitation signal frequencies measured at room temperature by means of the aixACCT Analyzer 2000 system. The coercive voltage V_c clearly increases with frequency. The log–log plot of V_c versus frequency gives, to good approximation, a straight line over the range of more than six orders of magnitude. So, empirically, the coercive voltage obeys the potential law

$$V_c \propto f^{\beta}. \tag{4}$$

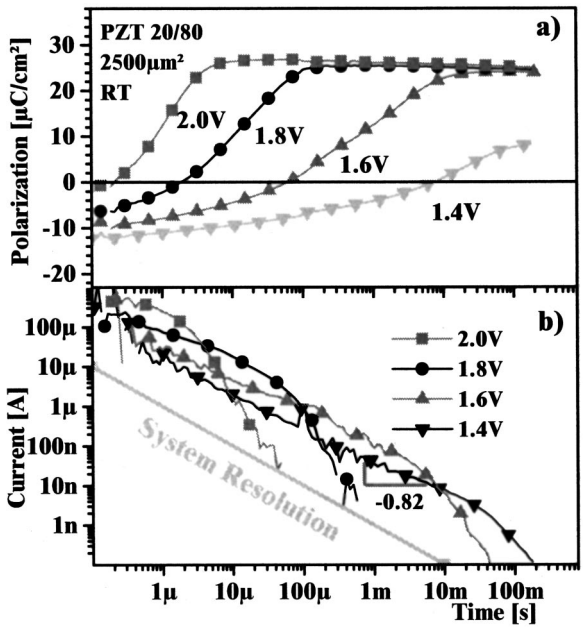

FIG. 4. (a) Polarization response of PZT thin film to excitation pulses with voltage levels close to coercive voltage. (b) Current response determined from the derivative of the charge response.

It should be noted that the shape of the loops does not change with frequency except that V_c is increased.

The voltage step measurements have been carried out with a 50 Ω voltage generator and a high precision picocoulombmeter at room temperature. In Fig. 4(a) the evolution of the polarization is plotted versus the time on a logarithmic scale. The voltage levels have been chosen in the range of the coercive voltage determined by the hysteresis measurements. As predicted by the Merz equations, the polarization reversal slows down with decreasing voltage level. When applying a 1.4 V voltage pulse, the polarization does not completely reverse in the investigated time range of 200 ms. The rather small increase of the voltage dramatically decreases the switching time. It clearly shows that the dielectric charging ($\tau_{RC_{diel}} < 10$ ns) is shorter than the time for polarization reversal. The voltage drop across the capacitor in this experiment is constant after approximately 100 ns and determined by the control properties of the operational amplifier of the coulombmeter. Additionally, the switching current, determined from the derivative of the charge response, is plotted on a logarithmic scale [Fig. 4(b)]. The current monotonically decreases and falls sharply approximately at the moment the saturated polarization is reached.

V. DISCUSSION

When the results from the hysteresis measurements and the pulse switching experiments of the PZT thin film sample are compared to the data of single crystals similarities, but also very pronounced discrepancies, can be observed. The frequency dependence of the coercive voltage follows Eq. (4), as theoretically calculated and found experimentally for TGS single crystals by Ishibashi. But in addition to the shift in the coercive voltage, in single crystals the shape of the $P-V$ loop is strongly affected by the change of the fre-

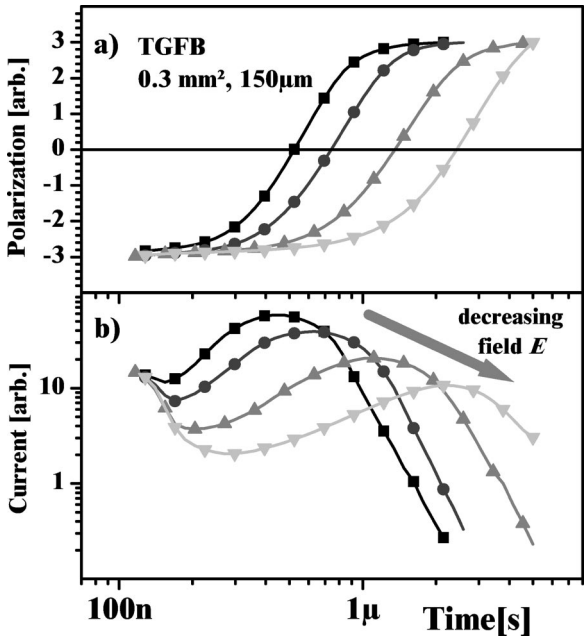

FIG. 5. Polarization switching current of TGFB single crystal with decreasing electrical field on a logarithmic scale.[10]

quency. This was not the case of the investigated PZT thin film sample. As already described, in the voltage step experiment, it was possible to switch the capacitor under a constant voltage excitation. The switching time can be fitted to Eq. (2), but the course of the current response differs significantly from that of single crystals. The typical switching hump in single crystals (see Fig. 1) cannot be observed in thin films [Fig. 4(b)]. To make the comparison clearer in Fig. 5(a), the TGFB switching data from Pulvari (see also Fig. 1) are plotted on a log–log plot. Again, it can be seen that the switching hump is pronounced in single crystals. In the current response of the thin film it is not possible to determine the characteristic value of the maximum current $i_{\max}$. However, the course of the integrated current per area, i.e., the polarization [Fig. 5(a)], is similar to the charge response of the thin film.

During the reversal, until the polarization has reached the opposite state, the current response shows a typical Curie–von Schweidler behavior and can be described by the following law

$$J \propto t^{-\alpha}, \tag{5}$$

where α is a constant and has a value of less or equal to one. When Eq. (5) is applied to the current response of the pulse of 1.4 V, we find a value for α of about 0.82. With increasing voltage this value slightly decreases.

The detection of this kind of current response leads to a different view of the polarization reversal since the Curie–von Schweidler behavior is found in all thin films, in dielectric[25,26] as well as in ferroelectric thin films.[27–30]

Two main models have been proposed for the Curie–von Schweidler relaxation, firstly a many-body interaction model which is based on the fact that the hopping motion of a charged particle always affects the motion of the neighboring charges.[31] And secondly, the distribution of relaxation times

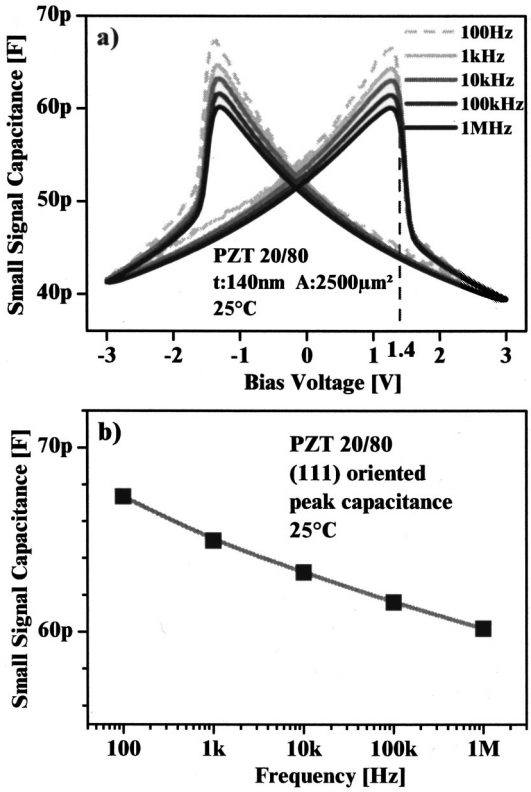

FIG. 6. (a) Small signal capacitance of PZT thin film during a bias voltage sweep of one cycle per minute (oscillator amplitude 50 mV_{rms}). (b) Capacitance of the right peak from (a).

model which is based on a superposition of Debye-type relaxations with a large distribution of relaxation times which may be caused by a variation in the charge transport barrier, for example at the grain boundaries.[32] However, the latter model has the drawback that it cannot describe the small temperature dependence of the relaxation current in dielectric thin films.

The Curie–von Schweidler law in nonferroelectric materials behavior leads to a linear dispersion in the frequency regime[33] which reads as

$$\epsilon = \epsilon_\infty + k_0(\omega^{\alpha-1}), \tag{6}$$

where ϵ_∞ is the permittivity at very high frequencies, k_0 a constant, and α being the same constant as in Eq. (5).

In principle, this correlation can also be observed in ferroelectric PZT thin films. In Fig. 6(a), the small signal capacitance measured by means of a HP4284A LCR meter (oscillator level 50 mV), is plotted versus the applied bias voltage. The bias was slowly swept at approximately one cycle per minute. This has been repeated with different frequencies. The peak in the value of the capacitance coincides with the coercive voltage of a low frequency hysteresis curve.[24] The capacitance in the saturated state, here at 3 V, is not frequency dependent, but the peak capacitance at the bias voltage of about 1.35 V shows a distinctive dispersion [see Fig. 6(b)]. This bias level is approximately the value of the voltage of 1.4 V that has been applied during the pulse measurement. So, we find a similar electrical behavior in ferroelectric films as in non ferroelectric films which have no

domains at all, with a value of α which is significantly smaller than one. This value leads to this rather high dispersion compared to BST films, e.g., prepared by metalorganic chemical vapor deposition where this value is close to one.[4]

VI. CONCLUSIONS

The ferroelectric polarization reversal in thin films of PZT can be slowed down to the range of milliseconds by applying voltage step levels of about the coercive voltage. The comparison of the current response to the polarization switching current of single crystals shows that they totally differ. The transient current of the thin film cannot be explained by the classical theory of nucleation and growth of opposite domains. Rather the current response obeys the Curie–von Schweidler law which is applicable to all kinds of electroceramic thin films, ferroelectric as well as nonferroelectric. Additionally, the small signal capacitance measurement of the ferroelectric film shows a distinct similarity to the behavior of nonferroelectric thin films. The presented data strongly suggest that it is not the domain walls and their motion which are decisive for the polarization switching but polarization processes with a broad distribution of relaxation times.

The physical origin of these processes has not yet been fully elucidated but some models have been proposed[34] which can describe this behavior in noncrystalline materials.

ACKNOWLEDGMENTS

The authors would like to acknowledge Professor G. Arlt and R. Meyer from University of Aachen, W. Hartner, G. Schindler, and M. Kastner from Infineon Tech. for fruitful discussions, and T. Schneller and R. Gerhardt for the support of the sample preparation. This work was supported by the German Ministry of Education and Research BMBF (Contract No. 03N60075).

[1] S. S. Eaton, D. B. Butler, M. Parris, D. Wilson, and H. McNeille, 1988 IEEE International Solid-State Circuits Conference, Digest of Technical Papers, pp. 130–131, 329.
[2] C. A. Paz de Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott, and J. F. Scott, Nature (London) **374**, 627 (1995).
[3] J. F. Scott and C. A. Paz de Araujo, Science **246**, 1400 (1989).
[4] J. D. Baniecki, R. B. Laibowitz, T. M. Shaw, P. R. Duncombe, D. A. Neumayer, D. E. Kotecki, H. Shen, and Q. Y. Ma, Appl. Phys. Lett. **72**, 498 (1998).
[5] P. K. Larsen, G. L. M. Kampschöer, M. J. E. Ulenaers, G. A. C. M. Spierings, and R. Cuppens, Appl. Phys. Lett. **59**, 611 (1991).
[6] P. K. Larsen, R. Cuppens, and G. J. M. Dormans, in *Science and Technology of Electroceramic Thin Films, Applied Sciences*, Vol. 284, edited by O. Auciello and R. Waser (Kluwer, Dordrecht, 1995), pp. 201– 221.
[7] W. J. Merz, Phys. Rev. **95**, 690 (1954).
[8] E. Fatuzzo and W. J. Merz, *Ferroelectricity, Selected Topics in Solid State Physics* (North–Holland, Amsterdam, 1967).
[9] J. Fousek and B. Březina, Czech. J. Phys., Sect. B **10**, 511 (1960).
[10] C. F. Pulvari and W. Kuebler, J. Appl. Phys. **29**, 1742 (1958).
[11] V. Shur, E. Rumyantsev, and S. Makarov, J. Appl. Phys. **84**, 445 (1998).
[12] H. Orihara, S. Hashimoto, and Y. Ishibashi, J. Phys. Soc. Jpn. **63**, 1031 (1994).
[13] S. Hashimoto, H. Orihara, and Y. Ishibashi, J. Phys. Soc. Jpn. **63**, 1601 (1994).
[14] Y. Ishibashi and H. Orihara, Integr. Ferroelectr. **9**, 57 (1995).
[15] A. N. Kolmogorov, Izv. Akad. Nauk SSR Ser. Fiz. Mat. Nauk **6**, 355 (1937).
[16] M. Avrami, J. Chem. Phys. **7**, 1103 (1939).
[17] M. Avrami, J. Chem. Phys. **8**, 212 (1940).
[18] M. Avrami, J. Chem. Phys. **9**, 17 (1941).
[19] V. Y. Shur, in *Ferroelectric Thin Films: Synthesis and Basic Properties, Ferroelectricity and Related Phenomena*, Vol. 10, edited by C. A. Paz de Araujo, J. F. Scott, and G. W. Taylor (Gordon and Breach, Amsterdam, 1996), Chap. 6, pp. 153–192.
[20] P. K. Larsen, G. J. M. Dormans, G. J. Taylor, and P. J. van Veldhoven, J. Appl. Phys. **76**, 2405 (1994).
[21] R. Waser, O. Lohse, M. Grossmann, D. Bolten, U. Boettger, and S. Tiedke, in *Ferroelectric Thin Films VIII* (Materials Research Society, Warrendale, Pa., 2000), Vol. 596.
[22] J. F. Scott, Intger. Ferroelectr. **12**, 71 (1996).
[23] I. W. Chen and Y. Wang Appl. Phys. Lett. **75**, 4186 (1999).
[24] O. Lohse, D. Bolten, M. Grossmann, R. Waser, W. Hartner, and G. Schindler, in *Ferroelectric Thin Films VI*, edited by R. Treece, R. Jones, C. Foster, S. Desu, and I. Yoo (Materials Research Society Warrendale, Pa., 1998), Vol. 493, pp. 267–78.
[25] R. Waser, in *Science and Technology of Electroceramic Thin Films, Applied Sciences*, Vol 284, edited by O. Auciello and R. Waser (Kluwer, Dordrecht, 1995), pp. 223–248.
[26] M. Schumacher, G. W. Dietz, and R. Waser, Integr. Ferroelectr. **10**, 231 (1995).
[27] X. Chen, A. I. Kingon, L. Mantese, O. Auciello, and K. Y. Hsieh, Integr. Ferroelectr. **3**, 355 (1993).
[28] A. K. Tagantsev, A. L. Kholkin, E. L. Brooks, and N. Setter, Integr. Ferroelectr. **10**, 189 (1995).
[29] M. Schumacher, S. Manetta, and R. Waser, J. Phys. IV **8**, 117 (1998).
[30] M. Schumacher and R. Waser, Integr. Ferroelectr. **22**, 109 (1998).
[31] L. A. Dissado and R. M. Hill, J. Mater. Sci. **16**, 1410 (1981).
[32] H. Kliem, IEEE Trans. Electr. Insul. **24**, 185 (1989).
[33] A. K. Jonscher, *Universal Relaxation Law, Dielectric Relaxation in Solids* (Chelsea, London, 1996).
[34] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials, Monographs on Physics* (Clarendon, Oxford, 1971).